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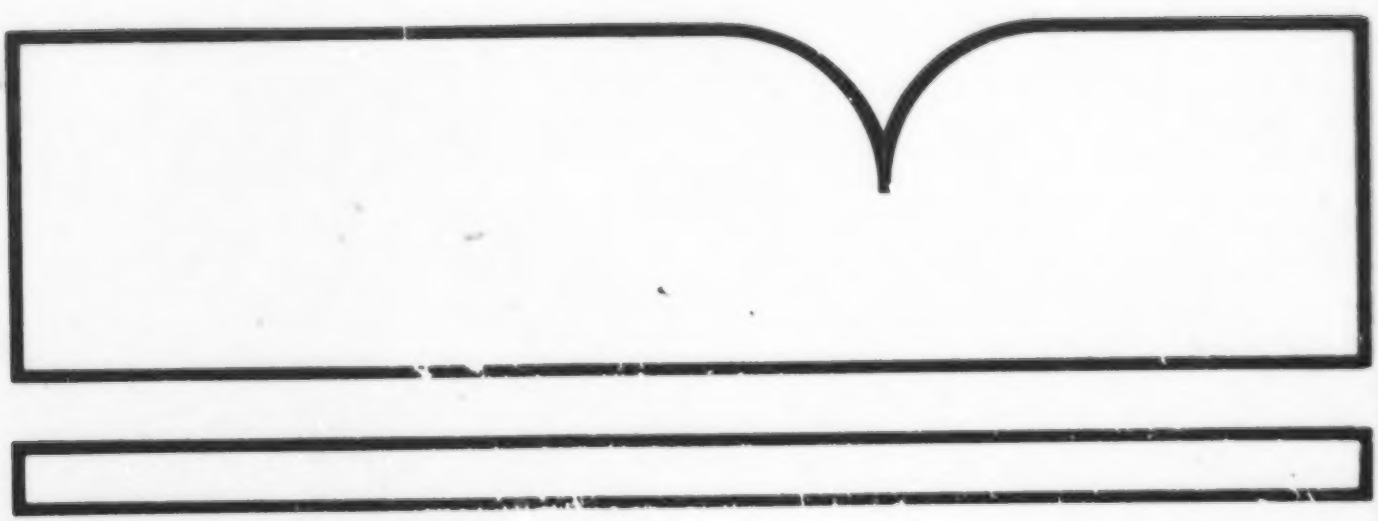

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SURROGATE COMPOUNDS AS INDICATORS OF HAZARDOUS WASTE INCINERATOR PERFORMANCE

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ABSTRACT

Evaluation of hazardous waste incinerators for Resource Conservation and Recovery Act permits is a difficult and sometimes costly task. The Environmental Protection Agency is evaluating, in its research program, several chemical compounds which may be used to monitor incinerator destruction and removal efficiency and combustion conditions more effectively. This paper discusses the research aimed at developing reliable and cost-effective methods for trial burns, and permit compliance monitoring.

INTRODUCTION

Regulations promulgated under the Resource Conservation and Recovery Act (RCRA) have identified nearly 400 compounds [17] which, if present in a waste material, can cause it to be designated as a hazardous waste and be subject to the rigorous disposal requirements required by law. When wastes containing any of these compounds are incinerated, the regulations require that the major waste components (called principal organic hazardous constituents or POHCs) be destroyed and/or removed to at least 99.99% (destruction and removal efficiency or DRE). Hazardous waste streams are often extremely complex mixtures containing hundreds of compounds of various chemical classes. An analysis for POHC's and other major waste components on a continuing basis is a difficult, time consuming and expensive task.

Since 1979, the Hazardous Waste Engineering Research Laboratory of the USEPA has been intensively involved in research to assess the capabilities of incineration facilities to meet the RCRA standards. This research is currently directed toward identification of easily-monitored facility operating parameters which correlate with, or are surrogates for, system performance. From these efforts, we anticipate establishing a sound scientific basis for the selection of monitoring methods which would simplify and reduce costs of incinerator facility validations and permit compliance monitoring.

BACKGROUND

Much of the attention in thermal destruction research has centered on the incineration of chlorinated organic compounds. Of all the compounds listed as components of hazardous waste, chlorinated organics were given high research priority because they are the most common compounds found in waste and represent a large portion of incinerable wastes generated [11].

Because of the large number of these compounds efforts were initiated early in the research program to reduce the number under study to a manageable level. By selecting POHC's representative of the compounds most prevalent in priority waste categories and which were generated in largest amounts, twenty-eight compounds were initially selected for the research program [11].

A major element in HWERL's thermal destruction research program was to com-

are the relative performance of different types of incinerators, industrial boilers and kilns by means of conducting research trial burns to evaluate DRE. It readily became apparent, in the beginning of this program, that waste analysis and stack sampling was more complex and costly than expected. To simplify research trial burns and to keep sampling and analysis costs in line with the research program budgets, nine of the twenty-eight compounds were chosen for full scale evaluation tests in industrial boilers and processes and pilot scale research. These compounds are listed in Table 1. To be selected, the compounds had to meet the following criteria:

- easily detectable in stack emissions with existing Sampling and Analysis methods
- have high thermal stability for its chemical class
- representative of physical and chemical properties of priority wastes.

Table I

Compounds Selected for EPA Research Program

carbon tetrachloride
methylene chloride
trichloroethylene
perchloroethylene
chlorobenzene
hexachlorobenzene
pyridine
acetonitrile
toluene

SURROGATES FOR HYDROCARBONS AND HALOCARBONS

After initial field tests, it became apparent that (1) these compounds were not always present in wastes at the sites that were available for testing; (2) there were analytical problems using existing methods with methylene chloride, toluene, acetonitrile and pyridine. The solution to the first problem, was to "spike" or add a known amount of the desired compounds to the waste in order to measure destruction and removal efficiency (DRE). This approach, for the most part, worked well, except that other problems appeared, such as handling problems due to toxicity, lack of commercial availability and high cost of the spiked compounds. Because of the need for spiking compounds into the waste, and the problems just discussed, it was decided to choose compounds that minimized these problems. Additional selection criteria were added and were made more restrictive by requiring the compounds be [11, 18]:

- non-inflammable
- non-toxic
- commercially available at relative low cost
- high thermal stability
- not likely to be formed as a PIC (Product of Incomplete Combustion)

A group of compounds that fit these criteria are the FREONS, halogenated organic compounds which are commercially available. Table 2 lists some of the more common ones which fit the selection criteria and would simulate a range of POHC physical properties. At a workshop on surrogate's sponsored by the California Air Resources Board [12], Freon 113 was selected as the most promising of those on the list. Its volatility is low, it is miscible with most of the wastes under study, and is low in toxicity. Its chief use is as a degreasing solvent.

The incineration of FREON 113 has also been studied in Sweden, both in incinerators [2] and cement kilns [1]. The Swedish studies reported it to be easy to detect but difficult to destroy. Because of the ease of detection, destruction efficiencies could be determined to a very high degree.

Table 2

Trial Burn Surrogates

Compound	Boiling Point, ^{o}C
Freon 11	24
Freon 113	48
Freon 114	4
Freon 22B1	150

Since 1983, the USEPA has conducted five research trial burn tests to evaluate the feasibility of using Freon 113 as a surrogate for wastes; three of the tests were at cement plants, one at a lightweight aggregate production plant and the

fifth was at a facility processing montmorillonite clay. Table 3 summarizes the DRE results for each of the processes studied.

The DRE's of Freon 113 and the POHC's in the cement kiln and aggregate plants exceeded the incinerator standards of 99.99% DRE. In the test of the plant processing montmorillonite, Freon 113 was the only halogenated compound present at a significant concentration (>1000 ppm). Even though the process temperature was low, the DRE of Freon 113 was greater than 99.99% throughout the test. The results demonstrate that Freon 113 is as difficult to incinerate as other POHC's in the tests and that it could feasibly be used as a reliable surrogate for most wastes with volatile components.

The other Freons listed in Table 2 should be evaluated as potential surrogates for less volatile and even solid hazardous wastes. The physical state of the surrogate compound should be the same as the POHC under evaluation; e.g. Freon 11 and Freon 113 should be used for volatile POHC's and Freon 22B1 should be used for solid waste. Evaluation of these compounds and further testing of the Freon compounds will be conducted in EPA's pilot scale and laboratory research program to further document the reliability of this technique.

A DIFFERENT APPROACH

The use of Freons and other halogenated organics, used as spiked material in hazardous wastes, may solve many of the problems associated with conducting trial burns. Further improvements, such as a reduction in complexity of analysis requirements, test time, and the associated costs, would be benefits to both industry and government.

An approach which could conceivably accomplish the objectives of shorter test time and lower cost is to use an altogether different compound such as sulfur hexafluoride (SF_6) [12,18]. SF_6 is a gas which has been widely employed as a tracer in experiments studying atmospheric transport of pollutants [16], meteorology [13], and atmospheric chemistry [5, 7, 8, 10]. Its high thermal and chemical stability, which made it very useful in the above mentioned studies, make it attractive as a potential surrogate for use in hazardous waste incineration trial burns [12, 18]. In addition to these properites, it is non-toxic [9, 14] and is commercially available at relatively low cost [16].

Being a gas, SF_6 cannot be easily or accurately added as a "spike" to liquid or solid hazardous waste. It is most easily introduced into an incinerator or other device by adding it continuously to the combustion air. A potential drawback to this approach is that it may not "simulate" the combustion dynamics, matrix effects or waste form that a POHC experiences. However, it is only a presumption and a theoretical assumption that this method of addition may not be preferred [12]. The practicality and relative low cost of using SF_6 may override any concensus about its suitability as a surrogate.

As part of continuing evaluation of surrogates, the California Air Resources Board and the USEPA sponsored three tests where the feasibility of using SF_6 as a surrogate was investigated. The tests were conducted at a circulating bed combustor (CBC) [4], a dry-process cement kiln and an asphalt plant Table 4 lists the SF_6 destruction and removal efficiencies (DRE) from each test, and the temperature for each process. DRE's for the POHC's in these tests are not yet available. Further studies, specifically devoted to developing the relationship between POHC and SF_6 destruction, are needed before final conclusions can be

Table 3

Freon 113 Feasibility Test Results

Process	Freon 113 DRE	POHC DRE	Process Temperature, °C
Cement	>99.999	>99.996	1500
Aggregate	>99.9999	99.99992	1150
Montmorillonite	>99.99	--	650

Table 4

SF_6 Feasibility Test Results

Facility	DRE	Process Temp °C
Cement Kiln	>99.999%	1500
CBC*	90 - 99.99%	790 - 850
Asphalt Plant	99.3 - 99.8%	190

*Circulating Bed Combustor

drawn on the suitability of SF_6 as a surrogate.

The SF_6 destruction efficiency in the circulating bed combustor varied considerably and appeared to be a function of temperature. In the cement kiln test however, destruction was so complete that SF_6 could not be detected in the stack gas from the kiln. The destruction efficiency was calculated based on the detection limit of the GC/ECD used for the analysis. Freon 113 was also used as a surrogate for this test and its DRE was >99.99%.

The asphalt plant test was quite different from the other tests in that the SF_6 DRE was not very high and the values were confined to a very narrow range.

The significance of these results is that for a range of process temperatures, there is a range of SF_6 DRE. As these were feasibility tests for the evaluation of the concept, further work is needed to establish the relationship between hazardous waste and POHC destruction with SF_6 DRE.

A driving force which might spur further research is the ease with which SF_6 data was collected. By the third test, at the asphalt plant, the experimental protocol had been developed to the point where all of the necessary data could be collected in 4 hours of testing. More than 15 stack samples per hour were taken and analyzed on a semi-continuous basis.

Recently, analyzers developed for continuously monitoring SF_6 concentrations in air, have been used for atmospheric studies [3, 6, 15] and could potentially be adapted for use in stack gas analysis. This would enable a facility operator to have a continuous readout of SF_6 destruction and removal efficiency. Continuous monitors for SF_6 could also be used to monitor permit compliance on a real-time basis, a tool which environmental agencies do not yet have.

CONCLUSIONS AND RECOMMENDATIONS

Based on feasibility and proof of concept tests, certain Freon compounds and sulfur hexafluoride may prove to be useful surrogates for hazardous waste incineration and be used for permit compliance monitoring. Experiments showed that these compounds are easily introduced into the incineration systems, require relatively simple and low cost equipment such as GC/ECD and are amenable to on-site analysis.

Further work on developing and demonstrating the relationships between surrogate DRE and hazardous waste destruction is recommended. Laboratory and pilot plant research is needed to further develop sampling and analysis protocols, and to make direct comparisons of POHC DRE's with those of surrogates.

REFERENCES

1. Ahling, B., "Destruction of Chlorinated Hydrocarbons in a Cement Kiln," Environmental Science and Tehnology, 13(11):1377-1379, November 1979.

2. Ahling, B. and Wiberger, K., "Incineration of Freon TF," Swedish Institute for Water and Air Pollution Research, Report #B 648, Stockholm, Sweden, January 1982.

3. Baxter, R. A., Pankratz, D. and Tombach, I., "An Advanced Continuous SF_6 Analyzer for Real-Time Tracer Gas Dispersion Measurements from Moving Platforms," AV-TP 83/504, Aero-Vironment, Inc., Pasadena, CA, 1983.

4. Chang, D. P. Y., and Sorbo, N. "Evaluation of a Pilot Scale Circulating Bed Combustor with Surrogate Hazardous Waste Mixtures," USEPA Eleventh Annual Research Symposium on Land Disposal and Remedial Action, Incineration and Treatment of Hazardous Wastes, Cincinnati, Ohio, April 1985.

5. Dietz, R. N. and Cote, E. A., "Tracing Atmospheric Pollutants by Gas Chromatographic Determination of Sulfur Hexafluoride," Environ. Sci. Technology, 7:338, 1973.

6. Dietz, R. N. and Goodrich, R. W., "The Continuously Operating Perfluorocarbon Sniffer," BNL 28114, Brookhaven National Laboratory, Upton, NY, 1980.

7. Dietz, R. N. and Dabberdt, W. F., "Gaseous Tracer Technology and Applications," BNL 33585, Brookhaven National Laboratory, Upton, NY, 1983.

8. Dietz, R. N. and Senum, G. I., "Capabilities, Needs and Applications of Gaseous Tracers," BNL 35108, Brookhaven National Laboratory, Upton, NY, presented at Atmospheric Tracers Workshop, Sante Fe, N.M., May 1984.

9. Johnson, W. B., "Meteorological Tracer Techniques for Parameterizing Atmospheric Dispersion," J. Appl. Meteorol. 22: 931, 1983.

10. Lester, D. and Greenberg, L. A., "The Toxicity of Sulfur Hexafluoride," Arch. Ind. Hyg. Occupational Med. 2:348-349, 1950.

11. Mournighan, R. E., "Preliminary POHC Ranking and Test Matrix," EPA internal planning document, June 1981.

12. Report on Workshop on Incineration Surrogate Compounds, University of California-Davis to the California Air Resources Board, November 1983.

13. Saltzman, B. E., Coleman, A. I. and Clemons, C., "Halogenated Compounds as Gaseous Meteorological Tracers," Anal. Chem. 38:753, 1966.

14. Sax, N. I., "Dangerous Properties of Industrial Materials",Van Nostrand Reinhold, New York, 1984.

15. Simmonds, P. G., Lovelock, A. J. and Lovelock, J. E., "Continuous and Ultrasensitive Apparatus for the Measurement of Airborne Tracer Sub stances," J. Chromatogr. 126:3, 1976.

16. Swartz, S. E., Leahy, D. F. and Fink, S., "Aircraft Release of Sulfur Hexafluoride as an Atmospheric Tracer," Jour. APCA 35:555, May 1985.

17. Title 40, Code of Federal Regulations, Part 261, Appendix VIII.

18. Tsang, W., and Schaub, W. M., "Surrogates as Substitutes for Principal Organic Hazardous Constituents of Incinerator Operations," Second Conference on Municipal, Hazardous and Coal Wastes Management, Miami Beach, Florida, December 1983.